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## Reasons for formation of stable intermediate layer water-in-oil emulsions in tanks

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**Abstract.** The present paper describes the possible causes of a high stable intermediate layer emulsion in tanks. Detailed studies have revealed that the main ones are mixing of oil from different oil-bearing horizons, presence of mechanical impurities in oil emulsions, presence of refractory paraffin hydrocarbons with melting temperature up to 85 ° C in oil, use of oilfield chemistry reagents, long-term oil production technological chain according to the integrated well-to-settling tank approach, application of intensive hydrodynamic well production modes, dispersion in metering and pumping installations. It is therefore important to understand and appreciate the high stable emulsions formation involved in processing and disposing of oil waste.

Oil and gas companies are one of the main environmental pollution sources. Oil and petroleum products that have been released into the environment as a result of accidents in production, transportation, storage and processing are the cause of numerous environmental problems. The adverse effect of oil sludge on the environment and hydrocarbon raw materials non-renewability makes the issue of disposing be rated as highly relevant [1].

The need to remove water from oil due to several reasons:

- with the increase in water content in oil, its market value decreases, and in case of violation of GOST R 51858-2002 [2] (water content more than 1% by weight.) oil is not accepted for sale;
- salts dissolved in formation water cause corrosion of technological equipment;
- the presence of water in the oil leads to a violation of the technological mode of operation of distillation columns during oil refining at oil refineries;
- transportation of water as part of oil is not economically feasible due to the reduction in the capacity of oil pipelines.

In the oil industry, all technological processes of production, collection, treatment of oil, gas and water are associated with the need to study the properties of oil-water emulsions entering the oil treatment plant.

Water-oil emulsions are divided into three groups:

Group I is an emulsion of the reverse type ("water in oil"), in which the water content (dispersed phase) in oil (dispersion medium) varies from "traces" to 90-95 %. The properties of these oil-water emulsions determine the main technological parameters of the processes of oil production, in-field collection, separation and affect the choice of equipment and technological modes of oil dehydration.



Group II is a direct type emulsion ("oil in water"), which is formed as a result of the destruction of the reverse type emulsion during oil dehydration. In the production and collection of production of producing wells in high-watered fields in the case of low mineralization of formation waters and oils with a high content of naphthenic acids is the formation of stable emulsions of direct type. Such emulsions can be formed during the thermal effect on the oil reservoir.

Group III is a "multiple emulsion" in which the particles of the dispersed phase contain a dispersion medium in their composition. Such emulsions are difficult to destroy by known methods and are the cause of disruptions in the technological processes of oil preparation, accumulating in the settling equipment at the interface. In the scientific literature, there is another name for such emulsions – emulsions of intermediate layers or "trap oil". These emulsion systems are characterized by a high content of mechanical impurities stabilizers. To remove the multiple emulsion, the technological devices are cleaned and then these emulsions are dumped into barns or oil traps for their further processing or disposal.

Oil emulsions are mainly formed in places where there is intensive contact, mixing of oil and produced water:

- when lifting from the bottom to the wellhead, where oil and formation water due to continuously changing thermobaric conditions undergo phase transformations with the release of dissolved gases and paraffins from oil;
- in the wellbore, where as a result of gas release, the pressure decreases and the intensity of mixing of the oil and water phases increases, as well as the speed of movement of the formation products increases. The gas is released with such energy that it is enough to disperse the formation water in oil;
- on the moving parts of submersible pumps, fittings and valves. The formation of oil emulsions occurs intensively during the passage of watered oil through the nozzle; in commercial equipment when the pressure drops, gas pulsations, sudden changes in direction and diameter process piping occurs turbulization of gas-liquid flow of production wells, enhancing the dispersion of produced water in the oil. In addition, the deposition of paraffin on the inner surface of the process equipment leads to a decrease in the cross-section of pipelines and, consequently, to an increase in the flow rate of production of producing wells [2].

As a result of the basic process of oil dehydration and desalting, water treatment, acceptance operations, operations connected with technological installations cleaning it is considered inevitable that oil waste will emerge and accumulate. Such wastes termed secondary emulsions are: trap oils, intermediate layers emulsions in the tank oil sludge. Summarizing, such secondary emulsions are a mixture of all substandard oils with different properties accumulated over a sufficiently long operation period of oil-gathering stations, compared with the emulsions of incoming raw materials, in particular, with anomalously high aggregate stability. There are several reasons for stable secondary emulsions formation [3].

The first reason for which the intermediate layer emulsion formation occurs in the production site tanks is the mixture of oils from different oil-bearing horizons.

This reason can be considered on the example of the Vankor oil field territory (Northern and Southern dome-shaped reservoir), which covers a vast contiguous territory. The deposit is divided into two licensed sites. The crude oil producing formations are the deposits of YakII-VII Yakovlevsky oil-bearing formation and NkhI, NkhIII-IV Nizhnekhetsky oil-bearing formation.

The Vankor oils are withdrawn from two oil-bearing horizons: the Nizhnekhetskaya oil-bearing formation and the Yakovlevsky oil-bearing formation. The oils of the Nizhnekhetsky horizon are light, low-sulfur, low-resin, low-viscous, paraffin oils with a high pour point. The oils of the Yakovlevsky horizon are bituminous, low-sulfur, resin, viscous, low-paraffin with a low pour point from 46 to 80° C below freezing containing a large amount of mechanical impurities from 100 mg / dm<sup>3</sup> to 500-700 mg / dm<sup>3</sup>.

The second reason is the mechanical impurities presence in oil emulsions.

Accumulating at the boundary of phase section in oil preparation installations mechanical impurities associated with asphalt-resin and paraffin components form stable intermediate emulsion layers the appearance of which leads to the disruption of the demulsification technological process mode, deterioration of commercial oil quality and drained reservoir water. Their appearance reduces the reliability of the phase separation boundary control system and leads to the need to carry out the discharge of the intermediate layers from oil preparation installations.

The third reason providing high stability of intermediate layers is caused by presence of refractory paraffin hydrocarbons with melting point up to + 85 °C.

The paraffin crystals appearance in the formed deposits of the intermediate layer is due to:

- reducing oil flow temperature to the values at which it is possible to extract solid paraffins from oil, also temperatures difference matters much: with an increase in the difference between the ambient temperature and the oil flow the amount of decomposing paraffin increases proportionally;
- when increasing oil flow rate, the accumulation intensity of deposits at first increases due to the mass transfer increase and reaches the maximum and at a certain speed begins to subside since with increasing speed oil better keeps paraffin crystals in suspended condition and the possibility of detergency effect of the deposited paraffin increases;
- presence of resin-asphalt substances in the oil strengthens the process of paraffin deposits;
- oil component composition: the more yield of light fractions (boiling up to 350 °C), the more paraffin precipitation [4-65].

The fourth reason is oilfield chemistry reagents. Currently, the following chemical reagents are usually used at the facilities:

- corrosion inhibitors, they are fed into the annulus and well discharge lines in order to protect the tubing and oilfield equipment in oil-gathering system against corrosion;
- corrosion inhibitors having bactericidal properties, they are fed into the annulus and well discharge lines in order to suppress the sulphate-regenerating bacteria growth and protect the tubing and oil-field equipment in oil-gathering system against corrosion;
- corrosion inhibitors dispensed into the formation water to protect the process equipment against corrosion at the preliminary water discharge unit of the central collection point;
- salting inhibitors dispensed into the emulsion which comes to the preliminary water discharge unit of the central collection point to prevent salt deposits;
- paraffin inhibitors having depressant properties designed to prevent paraffin deposits as well as reduce oil viscosity when transporting.

Dispensed into commercial oil:

- solvents designed for detergency of asphalt-resin-paraffin deposits formed in the bottomhole formation zone and in the oil producing wells;
- demulsifiers dispensed continuously into the oil-water emulsion for oil dehydration and desalting at the inlet of the preliminary water discharge unit of the central collection point. Low concentration does not cause emulsion destruction; overdose leads to redispersion.

Due to wells treatment by the method of "salvo" injecting with corrosion inhibitors bactericides deteriorate oil quality and produced water. Technologies based on the supply of reagents in high concentrations experience a side effect. It is an increase in the proportion of fine water droplets in oil

and water quality deterioration due to oil emulsification and solubilization in water with low-molecular-mass surface-active components of the corrosion inhibitor.

Influence analysis of the corrosion inhibitors with working concentrations of 25 g / m<sup>3</sup> and impact concentrations of 500 g / m<sup>3</sup>, salting inhibitors with a concentration of 25 g / m<sup>3</sup>, paraffin inhibitors with a concentration of 200 g / t, solvents concerning demulsifying efficiency of the most common and widely used demulsifier SNPH-4315DV shows that combined use of corrosion inhibitors, paraffin inhibitors, solvents and demulsifier SNPH-4315DV increases the demulsifying activity of the latter, especially at the initial dehydration stage. However, as further studies have shown when using corrosion inhibitors according to the shock dosage technology the quality of prepared oil deteriorates, namely, the content of residual water increases from 0.4% to 1.7%, chloride salts from 53 mg/l to 218 mg/l [6].

The technologies of enhanced oil recovery mainly use high molecular weight polyacrylamide polymers of various grades and gel compositions based on chromium acetate.

Also, when geological and technological activities take place chemical reagents such as acids and alkalis are applied to increase oil formation recovery.

All these reagents, one way or another, fall into water-in-oil emulsion coming from the wells. And surfactants included in the demulsifiers composition are emulsion stabilizers.

The fifth reason is long-term oil production technological chain according to the integrated well-to-settling tank approach and application of intensive hydrodynamic well production modes, dispersion in metering and pumping installations.

Crude oil is supplied for preparation at the preliminary water discharge unit or is prepared at a central collection point. Pretreatment preliminary water discharge units and central collection point are intended for crude oil preparation in terms of a marketable condition, separation of reservoir products to produce oil-associated gas, collection and preparation of produced water with their subsequent supply to reservoir pressure maintenance system, metering and supply of commercial oil to tanks.

Analysis of oil treatment plants operations at various oil fields showed the presence of stable emulsions in process tanks.

The formation of the intermediate layer in the settling installations is described by the authors [7]. When entering the installation, the incoming reverse oil emulsion is crushed in the aqueous phase, with the formation of large oil drops with droplet water, which quickly float and are retained by a dense layer that has not had time to coalesce with oil drops. Large local oil formation with droplet water remaining in the aqueous medium form the lower sublayer of direct multiple emulsions the boundary of which from the aqueous phase forms the lower boundary of the intermediate layer.

When separating oil emulsions paraffin microcrystals, asphaltenes and resins are concentrated on the interface in capacitive oil installation. The main amount of mechanical impurities is also concentrated at the interface where the main volume accumulation of the most stable oil emulsions with incompletely destroyed water globules reservation shells occurs [8].

Currently most of Russia's largest oil fields are at the final development stage which complicates oil production and increases water cutting of well production. The extracted oil properties are changed; also a large amount of various origins oil sludge is accumulated. In addition, the use of various enhanced oil recovery methods leads to the formation of a large number of stable intermediate layers emulsions. Their formation leads to the disruption of technological process of oil preparation, deterioration of commercial oil quality and drainage water as well as an increase in the amount of oil waste disposing in particular reservoir type oil sludge.

As a result of analysis of reasons for formation of stable intermediate layer water-in-oil emulsions in tanks, it can be concluded that due to its multi-factor character the problem of formation of intermediate layer emulsion can be solved to a greater extent only at the final stage of oil preparation and transportation, namely, at the stage of oil settling in tanks which will consequently reduce the total volume of disposed oil sludge at the water treatment plant.

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